PB86-148459

Predictive Models: Permeation of Polymeric Membranes by Organic Solvents

Southern Research Inst., Birmingham, AL

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jan 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-148459

EPA/600/D-86/021
January 1986

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EPA Contract 68-03-3113

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CINCINNATI, OH 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-86/021		PB86 148459/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Predictive Models-Permeation of Polymeric Membranes by Organic Solvents	January 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
G. Sides, et.al.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southern Research Institute P.O. Box 55205 Birmingham, AL 35255	11. CONTRACT/GRANT NO. 68-03-3113
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Water Engineering Research Laboratory-Cl,OH Office of Research and Development U.S. EPA Cincinnati, OH 45268	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Protective clothing (for example, gloves, aprons, masks, and protective ensembles) is often constructed in the form of barrier polymeric membranes. Permeation testing, which is used frequently to screen candidate polymers for use as protective barrier, is expensive and time consuming--particularly when working with compounds as toxic and as subject to regulation as CW agents. We have recently reviewed the literature and developed an initial approach to the prediction of the diffusivities and solubilities of organic solvents in polymers. A brief review of the applicable theory will be presented. Predicted diffusivities and solubilities for several solvent/polymer combinations will be compared to experimental data.

This work was sponsored by the Environmental Protection Agency's Office of Research and Development and Office of Toxic Substances via Contract 68-03-3113 with SAIC.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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PREDICTIVE MODELS—PERMEATION OF POLYMERIC MEMBRANES BY ORGANIC SOLVENTS

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INTRODUCTION

During the past four years, approximately 2000 permeation tests have been conducted at Southern Research Institute. Because of the expense of conducting such tests—particularly with CW agents—models that would allow the prediction of permeation through polymeric materials and, thus, be useful for screening candidate protective materials are of interest. The work[1] reported here emphasized the prediction of permeation through unsupported, natural-rubber glove formulations because of the relative "purity" of these formulations (typically 93% latex) when compared to other formulations (for example, PVC-based gloves typically contain >40% plasticizer). Also, experimental solubilities and diffusion coefficients for various solvents in natural rubber are available.

APPLICABLE MASS-TRANSPORT THEORY

If it is assumed that Fick's laws of diffusion are valid, that the diffusion coefficient is independent of solvent concentration in the polymer, and that swelling of the polymer is negligible, then the permeation rate (J) for a solvent through a glove sample whose outer surface is in contact with the liquid solvent is given by:

$$J = (DS/\ell)\{1 + \sum_{m=1}^{\infty} 2\cdot\cos(\pi m)\cdot\exp(-m^2\pi^2 Dt/\ell^2)\} \qquad (1)$$

where D is the solvent diffusion coefficient, S is the solubility of the solvent in the polymer, and ℓ is the sample thickness. Thus, if the diffusion coefficient and solubility of the solvent in the polymer can be predicted by a model, then permeation-rate curves and other quantities of interest (for example, breakthrough times, lag times, and steady-state permeation rates) can be predicted. This simple model may also be modified to account for phenomena such as the generally observed concentration dependence of the diffusion coefficient.

SOLUBILITY PREDICTIONS

Two approaches to the prediction of solubility were attempted: Flory-Huggins theory (combined with the use of solubility parameters) and the UNIFAC-FV or UNIFAP theory developed by Fredenslund, Oishi, and Prausnitz. In both approaches, the assumptions were made that none of the polymer dissolved in the liquid phase (that is, the solvent remained pure) and that the standard state for the solvent in both the liquid phase and the polymer phase was the pure solvent (for which the activity, a_1, is unity). Thus, it

was only necessary to determine the solvent volume fraction in the polymer that yielded a_1=1 to predict the solubility of the solvent in the polymer.

If it is assumed that the molar volume of the solvent, v_1, is much less than the molar volume of the polymer, then the Flory-Huggins equation may be written:

$$\ln a_1 = \ln \phi_1 + (1-\phi_1) + \chi(1-\phi_1)^2 \qquad (2)$$

where χ is the Flory interaction parameter for the polymer/solvent system and ϕ_1 is the solvent volume fraction. At equilibrium, a_1=1 and Equation 2 may be written as:

$$0 = \ln \phi_1 + (1-\phi_1) + \chi(1-\phi_1)^2 \qquad (3)$$

Huggins suggested that χ is related to Hildebrand's solubility parameters for nonpolar systems:

$$\chi = (v_1/RT)\ (\delta_1-\delta_2)^2 \qquad (4)$$

where δ_1 and δ_2 are the solubility parameters for the solvent and polymer, respectively. In this work, Hansen's so-called 3-component or 3-dimensional solubility parameters were used to calculate the separation in solubility space, A, which was substituted for the difference $(\delta_1-\delta_2)$ in Equation 4 to make the theory more applicable to polar systems. Three approaches to the calculation of A have been reported:[2-4]

$$A = [(\delta_d^p-\delta_d^\ell)^2 + (\delta_p^p-\delta_p^\ell)^2 + (\delta_h^p-\delta_h^\ell)^2]^{1/2} \qquad (5)$$

$$A' = [4(\delta_d^p-\delta_d^\ell)^2 + (\delta_p^p-\delta_p^\ell)^2 + (\delta_h^p-\delta_h^\ell)^2]^{1/2} \qquad (6)$$

$$A'' = [(\delta_d^p-\delta_d^\ell)^2 + 0.250(\tau^p-\tau^\ell)^2]^{1/2} \qquad (7)$$

where the p and ℓ superscripts refer respectively to the polymer and the liquid solvent, δ_d is for dispersion forces, δ_p is for polar effects, δ_h is for hydrogen bonding, and $\tau = (\delta_p^2 + \delta_h^2)^{1/2}$.

Solubilities calculated for a series of solvents in natural rubber are given in Table 1. These calculated solubilities correlate poorly with experimental solubilities reported by D.R. Paul et al.[5] For this reason and because the UNIFAP approach to calculating solubilities appeared more promising, attempts to use Flory-Huggins theory and solubility parameters were discontinued.

Fredenslund's UNIFAC theory is based on the use of functional-group interaction parameters calculated from experimental phase-equilibrium data to determine the activities of each component in mixtures. Oishi and Prausnitz extended this work to include free-volume theory and, thus, to make it applicable to polymer/solvent systems. A software package (UNIFAP) to conduct calculations that enable the prediction of solvent solubility in polymers is available from Prausnitz. The primary input data are the solvent and polymer densities at the temperature of interest and the identity of the functional groups in the solvent and the polymer.

A comparison of solubilities calculated using UNIFAP theory with D.R. Paul's experimental data for a series of solvents in natural rubber and four other polymers is given in Table 2. The typical agreement is within a factor of five or better.

The data in Table 2 reveal two problems with UNIFAP. First, it yielded predictions of total miscibility for a number of solvents, which experimentally showed large but finite solubilities. This occurs because UNIFAP does not consider crosslinking. Secondly, the database of interaction parameters is limited to a relatively small set of functional groups. Thus, the interaction parameters for functional groups needed to define given polymers or solvents may not be available.

DIFFUSION-COEFFICIENT PREDICTIONS

This work emphasized the prediction of solubility. However, C.W. Paul's model[6] based on free-volume theory was used to estimate the concentration-dependence of the diffusion coefficients for benzene and n-heptane in natural rubber. Paul's model requires less experimental data (that is, physical properties) than other free-volume-theory models, such as that published by Vrentas and Duda.[7]

A comparison of the predicted concentration-dependence of the diffusion coefficient for benzene in natural rubber is shown in Figure 1. Although the values of the maximum in both curves are in good agreement, the locations of the maximum relative to the solvent volume fraction are not. The initial work in the application of the Paul model will continue in an attempt to eliminate the discrepancy shown.

PREDICTION OF A PERMEATION-RATE CURVE

The solubility predicted for benzene in natural rubber using UNIFAP and the diffusion-coefficient curve given in Figure 1 (despite its disagreement with experimental data) were used to predict the permeation rate as a function of time for a 0.046-cm thick glove (Figure 2). This curve was calculated using the Crank-Nicholson implicit finite differences approach to solving Fick's second law of diffusion with a "look-up" table for the diffusion coefficient. The agreement between the predicted curve and that derived from data reported by Weeks and McLeod[9] should be considered somewhat fortuitous but, nonetheless, encouraging.

CONCLUSION

The feasibility of the prediction of the performance of a chemical-protective glove has been demonstrated in this work. However, much effort remains to develop a model that will be generally applicable to a broad range of protective gloves and solvents.

ACKNOWLEDGMENTS

Other Institute staff contributing to this work included W.J. Jessen, R.F. Collison, J.W. Gibson, J.P. English, B.L. Reaves, and M.D. Howard. The authors also acknowledge the support of J.P. Meade (JRB Associates) and K.F. Wong and M.D. Royer (US Environmental Protection Agency) under Contract 68-03-3113. [This manuscript does not necessarily reflect EPA policy.]

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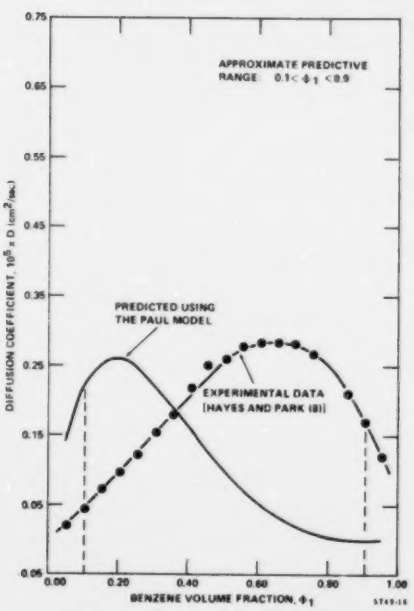

Figure 1. Diffusion coefficient of benzene in natural rubber as a function of volume fraction.

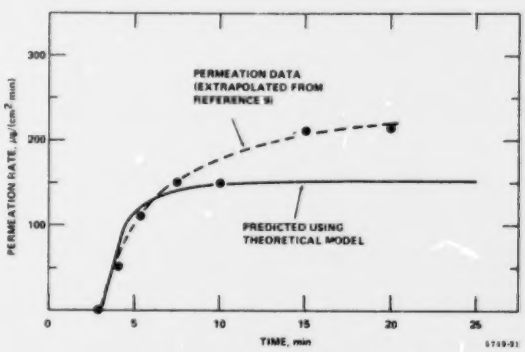

Figure 2. Comparison of predicted and experimental permeation-rate curves for benzene through natural rubber.

TABLE 1. SOLUBILITIES CALCULATED FOR VARIOUS SOLVENTS IN NATURAL RUBBER[a] (BASED ON FLORY-HUGGINS THEORY AND SOLUBILITY PARAMETERS)

Solvent	Literature solubility[b]	Calculated solubility[c,d]		
	$10^5 \times C_{exp}$	$10^5 \times C_1$	$10^5 \times C_1'$	$10^5 \times C_1''$
Methanol	4.92	3.21	1.88	392
Ethanol	8.59	5.37	3.21	394
Isopropanol	52.8	18.7	9.21	604
n-Butanol	125	14.3	6.99	475
n-Pentanol	130	34.5	13.7	724
Benzyl alcohol	142	35.0	35.0	2630
n-Propanol	146	9.33	5.25	439
Acetone	169	64.2	26.7	*
2-Ethyl-1-butanol	259	28.1	8.48	483
t-Pentanol	437	2.23	0.110	92.9
Diethyl carbonate	636	*	858	*
Methyl ethyl ketone	713	69.9	30.8	*
Ethyl acetate	766	1400	151	*
n-Propyl acetate	1270	28.4	1.74	363
n-Hexane	1540	8.57	1.15	152
n-Heptane	1580	5.71	1.00	135
Tetralin	3330	266	157	*
Cyclohexane	3380	39.7	25.9	1380
Cyclohexanone	3410	489	429	*
Toluene	3870	299	284	*
Tetrachloroethylene	4240	136	127	*
Carbon tetrachloride	5370	94.8	88.9	*
Trichloroethylene	5690	*	*	*

[a]The concentrations (solubilities) reported are in units of moles/cm^3 of unswollen polymer at 298 K.

[b]These values are calculated from the experimental volume-fraction data reported by D.R. Paul.

[c]These values are calculated using Flory-Huggins theory. The term C_1 means that Equation 5 was used to calculate the separation in solubility space; C_1' corresponds to Equation 6; and C_1'' corresponds to Equation 7.

[d]The symbol "*" means that no solubility could be calculated, because these systems are predicted to be miscible in all proportions.

TABLE 2. COMPARISON OF SOLUBILITIES CALCULATED USING THE UNIFAP MODEL OR OBTAINED EXPERIMENTALLY WITH MANUFACTURERS' CHEMICAL-RESISTANCE GUIDELINES[a,b]

Polymer	Solvent	$10^5 \times C_{uni}$	$10^5 \times C_{exp}$	Degradation rating	Permeation rating
Natural rubber	Methanol	26.5	4.92	E	E, NN
	Ethanol	42.4	8.59	E	VG, NN
	Isopropanol	81.6	52.8 (81.4)	E	E, NN
	n-Butanol	93.3	125	E	G
	n-Pentanol	103	130	NA	NA
	Benzyl alcohol	27.5	142	NA	NA
	n-Propanol	100	146	E	VG
	Acetone	185	169 (263)	E	F, NN
	2-Ethyl-1-butanol	114	259	NA	NA
	t-Butanol	81.5	414	NA	NA
	t-Pentanol	96.9	437	NA	NA
	Diethyl carbonate	202	636	NA	NA
	Methyl ethyl ketone	271	713	G	P, NN
	Ethyl acetate	411	766	G	G, NN
	n-Propyl acetate	581	1270	F	F, NN
	n-Hexane	*[c]	1540	NR	NA
	n-Heptane	*	1580	NA	NN
	Tetralin	*	3330	NA	NA
	Cyclohexane	*	3380 (3190)	NA	NN
	Cyclohexanone	*	3410	NA	NA
	Toluene	*	3870 (3480)	NR	NN
	Tetrachloroethylene	*	4240	NA	NN
	Carbon tetrachloride	*	5370	NR	NN
	Trichloroethylene	*	5690	NA	NN
Butyl rubber	Acetone	322	(78.7)	NA	NA
	Cyclohexane	*	(3240)	NA	RR
	Isopropanol	29.7	(6.8)	NA	NA
	Toluene	*	(1920)	NA	NA
Neoprene rubber	Acetone	*	(696)	G	F, NN
	Cyclohexane	*	(1040)	NA	NN
	Isopropanol	69.8	(95.5)	E	E
	Toluene	--[d]	(3410)	NR	NN
Nitrile rubber	Acetone	--	(3130)	NR	NN
	Cyclohexane	--	(117)	NA	RR
	Isopropanol	--	(389)	E	E, RR
	Toluene	--	(1560)	F	F, NN
Poly(vinyl chloride)	Acetone	*[e]	(--)[f]	NR	NN
	Cyclohexane	*	(--)	NA	NN
	Isopropanol	49.5	(--)	G	E
	Toluene	*	(--)	NR	NN

[a] The units of the calculated equilibrium solubilities, C_{uni}, and the experimental solubilities, C_{exp}, are moles/cm^3.

[b] The values in parentheses under the column labeled "$10^5 \times C_{exp}$" were determined during immersion tests conducted under the current effort; the other data under this heading were calculated from data reported in Reference 5.

[c] The symbol "*" in this column means that an activity of one was achieved only for a solvent volume fraction equal to one. (That is, the solvent and the polymer are predicted to be miscible in all proportions.)

[d] The symbol "--" in this column means that no interaction parameters were available for the polymer/solvent pair indicated.

[e] The UNIFAP solubilities for solvents in poly(vinyl chloride) were based on the polymer structure alone; the presence of plasticizer was not considered.

[f] The symbol "--" in this column means that weight loss was observed in the immersion tests with poly(vinyl chloride).